SINOMENIN UND DISINOMENIN. XXIII.[1] UEBER DIE IDENTITAET VON β-TETRAHYDRODESOXY-CODEIN UND DIHYDRO-THEBAKODIN.

Von **Kakuji GOTO** und **Shingo MITSUI.**

Eingegangen am 9. Januar 1931. Ausgegeben am 28. Februar 1931.

Kondo und Ochiai[2] haben zuerst das Sinomenin (I) der Clemmensenschen Reducierung unterworfen und berichtet dass dabei Desoxy-tetrahydrosinomenin (III), die *d*-Form von Dihydro-thebakodin, entstanden war. Als Beweise dafür dass die Phenolgruppe in 4 fortreduciert war, führten sie die Tatsachen an, dass die neue Base alkaliunlöslich war und keine Eisenchloridreaktion mehr zeigte. Als Beweis des Vorhandenseins einer sekundären Alkoholgruppe, ersetzten sie die letztere durch Chlor, obgleich das Chlorgehalt dieses Chlorids viel niedriger als das berechnete war.

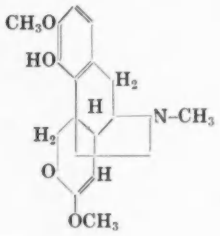
Diese Angabe war etwas erstaunlich, weil nach Ihnen das Sinomenin durch Zn-Amalgam schon seinen Phenolhydroxyl einbüsste, während seine Ketongruppe nur zum Alkohol reduciert wurde. Dieses Verhältnis veranlasste den Einen der Autoren[3] diese Reduktion zu wiederholen und er hat gefunden dass dabei nicht *d*-Dihydrothebakodin, sondern Desoxo-demethoxy-dihydro-sinomenin (II), d.h. die *d*-Form von β-Tetrahydrodesoxycodein gebildet wurde. Das Vorhandensein des Phenolhydroxyls in dieser Desoxo-demethoxybase wird durch die unveränderte Diazoreaktion verratet. Die Tatsache, dass in dieser Verbindung die Ketongruppe zum Methylen reduciert wurde, geht aber auch aus ihrer anderen Darstellungsweise aus Demethoxydihydrosinomenin durch Phosphorpentachlorid und nachfolgende Reduktion hervor (siehe Versuchsteil).

Dann wendeten Kondo und Ochiai[4] einer neuen Auffassung zu, d.h. Dihydrothebakodin und β-Tetrahydrodesoxycodein eine und dieselbe Substanz sein müssen. Die Ähnlichkeit dieser zwei Substanzen ist sehr auffallend und man kann bloss aus den äusseren Eigenshaften, wie Krystallform, Schmelzpunkt, Drehungsvermögen u. s. w. nichts Sicheres beschliessen. Doch jederman, der die Originale[5] von Speyer und Siebert liest, kann nicht die Selbständigkeit von Dihydrothebakodin bezweifeln. Der Ersatz

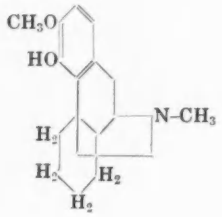
(1) Kitazato u. Goto, Die Sulfonierung der Alkaloide ist als XXII Mitteilung zu betrachten.
(2) *Ann.*, **470** (1929), 227; *Ber.*, **63** (1930), 646.
(3) Dieses Bulletin, **4** (1929), 244.
(4) *Ber.*, **63** (1930), 646.
(5) *Ber.*, **54** (1921), 1526.

von dem Hydroxyl mit Chlor mittelst Phosphorpentachlorids könnte nicht so leicht ausgeführt werden, wenn er einen Phenolhydroxyl darstellte. Der Schluss, zu dem Kondo und Ochiai gelangt haben, verlangt natürlich einen weiteren Stütz.

Wir versuchten das Problem aus einer anderen Seite auzugreifen. Glücklicherweise haben wir Demethoxy-dihydrosinomenin (V) und Desoxo-demethoxy-dihydrosinomenin (II) in einer genügenden Menge in Hand gehabt. Wenn wir diese zwei Substanzen der Tafelschen Elektro-reduktion unterwerfen, um zu sehen, ob dadurch der Phenolhydroxyl fortreduciert wird, so können wir darüber einen sicheren Schluss ziehen.



I.



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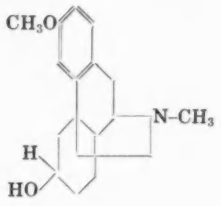


III.

IV.[1] Dihydrosinomenin—CH_2-CO-$C(OCH_3)$H-CH_2—

V.[2] Desmethoxy-dihydro-sinomenin (*d*-Dihydrothebainon)
—CH_2-CO-CH_2-CH_2—

VI.[3] Demethoxy-dihydro-sinomeninol—CH_2-CHOH-CH_2-CH_2—

VII.[4] Sinomeninol—CH_2-C(OH)H·$C(OCH_3)$=CH—

VIII.[4] Dihydrosinomeninol—CH_2-C(OH)H·$C(OCH_3)$H-CH_2—

IX.[5] Sinomeninhydrat—CH_2-CO-$C(OCH_3)$(OH)-CH_2—

X.[5] α-und β-Demethoxy-sinomeninhydrat—CH_2-CO-CH(OH)-CH_2—

Die Resultate dieser Reduktion werden in der folgenden Tabelle 1 zusammengefasst.

(1) Dieses Bulletin, **5** (1930), 282.
(2) Dieses Bulletin, **4** (1929), 244.
(3) Dieses Bulletin, **5** (1930), 282.
(4) Ibid.
(5) Dieses Bulletin, **4** (1929), 271.

Tabelle 1.

Substanz	Angewandte Menge (gr.)	Katholyt (25% H_2SO_4)	Zeitdauer (Stunden)	Stromkonz. per 100 c.c. (Amp.)	Ausbeute
[V]+[VI]*	8	160	3	9~9.5	[II] 1.2 gr. [VI] 2.7 gr.
[II]	6.8	140	3.5	10	[II] 60%
[VIII]	7.3	160	5	9.2	[VIII] 70%
[VII]	4.0	80	5	9~12	[VII] 75%
[IV]	10	150	4.5	10	[IV] 90% [VIII] sehr wenig
[I]	10	150	4	10.7	[IV] 3.4 gr.

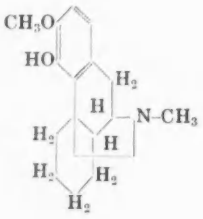
* Dass dieses Gemisch aus fast gleicher Menge von Demethoxy-dihydro-sinomenin und Demethoxy-dihydro-sinomeninol bestand, wurde durch Isolierung von Jodmethylat und Semicarbazon von dem ersteren quantitativ nachgewiesen [Dieses Bulletin, 5 (1930), 288]. Es ist klar, daher, dass 2.7 gr. von [VI] nicht durch die Reduktion von [V] gebildet wurden, sondern die unverändert zurückgewonnenen Substanz darstellten.

Die Ausbeuten, die in Prozentgehalt ausgedrückt wurden, bezeichnen die Mengen der unverändert zurückgewonnenen Substanzen.

In diesen acht Versuchen, haben wir in keinem Fall die Alkoholbase isoliert, welche dem Dihydrothebakodin von Speyer und Siebert entspricht. Diazo-reaktion wurde sogar am jeden einzelnen krystallisierten Anteil geprüft, aber wir beobachteten keine Verminderung. Wir sind daher auch geneigt zu denken, dass Dihydro-thebakodin eine und dieselbe Substanz mit β-Tetrahydrodesoxykodein darstelle.

Natürlich ist die Reduktionsfähigkeit in der elektrolytischen Methode stark von der Natur von den Elektroden, vom elektrischen Strom, Temperatur u.s.w. abhängig und wir dürfen nicht einen voreiligen Schluss ziehen. Die Möglichkeit dass in Speyer und Siebertschem Fall, der Phenolhydroxyl tatsächlich fortreduciert worden war, ist nicht ausgeschlossen. Doch wird unserer Schluss auch dadurch unterstützt dass die des-N-Methylbase von Desoxo-demethoxy-dihydro-sinomenin schmilzt bei demselben Grad wie die des-N-Methyl-base von Dihydrothebakodin und dass der stickstofffreie Körper von dem ersteren fast denselben Schmelzpunkt wie der des lezteren besitzt. Diese frappante Übereinstimmung von Schmelzpunkt finden wir auch bei den des-N-Methyl-basen von Demethoxy-dihydrosinomenin und von Dihydrothebainon, welche beide ein optisches Paar[1] zueinander sind.

(1) Dieses Bulletin, **4** (1929), 271.



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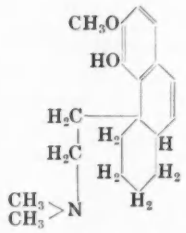

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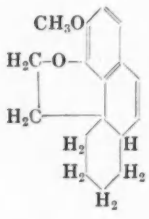


XIII.

Die Schwerreducierbarkeit von dem sekundären Alkohol auf dem elektrolytischen Weg führte uns zu prüfen, ob dasselbe Verhältnis in der Clemmensenschen Reduktion besteht. Schon lange hat Clemmensen[1] gezeigt dass der Hydroxyl nur dann fortreduciert wird, wenn er vicinal zu einem Keton steht und dass der Hydroxyl, der etwas entfernt davon liegt, wie bei ω-Aceto-propylalkohol, unberührt bleibt. Die Resultate unserer Versuche sind mit den obigen gut vereinbar und in der Tabelle 2 zusammengefasst.

Tabelle 2.

Substanz	Ausbeute	Unveränderte Subst. zuruckgewonnen.
1. Sinomenin.	25%	—
2. Dihydro-sinomenin.	30%	—
3. Demethoxy-dihydro-sinomenin.	30%	—
4. Sinomenin-hydrat	30%	—
5. α-Demethoxy-sinomenin-hydrat	50%	—
6. β-Demethoxy-sinomenin-hydrat	30% (Schmp. 141°)	—
7. Sinomeninol	—	60%
8. Dihydrosinomeninol	—	60%

Die Tatsache, dass α-Demethoxysinomeninhydrat auch zu Desoxodemethoxy-dihydrosinomenin reduciert wurde, zeigt dass in dieser Substanze die Hydroxylgruppe mit dem Keton benachbart sein muss. Folglich wurde dadurch die Auffassung seiner Muttersubstanz, Sinomeninhydrats, als ein Semiacetal wieder auch einigermassen bestätigt.

(1) *Ber.*, **52** (1914), 681.

In ihren Abhandlung, haben Kondo und Ochiai die Bezeichung Dihydrothebainan[1] für die β-Tetrahydrodesoxycodein und Dihydrothebakodin vorgeschlagen. Doch denken wir dass der Name etwas ungepasst sei. Der Name Thebainon ist schon lange in der Literature eingebürgert, und man versteht jetzt allgemein dass in Thebainon die Methyl-amino-äthyl-seitenkette in einem anderen Ort als beim Dihydrothebainon angehängt ist, wie es C. Schöff sehr wahrscheinlich gemacht hat. Wir mögen hier den Name Dihydro-eu-thebainan vorschlagen, weil die Tatsache dass die genannte Seitenkette in Thebain und Dihydrothebainon in demselben Punkt C(13) verknüpft ist jetzt allgemain anerkannt.

Beschreibung der Versuche.

I. Tafelsche Reduktion von Sinomenin und Seiner Derivaten. Die Resultate sind in der Tabelle 1 zusammengefaszt. Als Beispiele, sei die Reducierung von Demethoxy-dihydrosinomenin (V) hier angeführt werden. Wegen der Erspärnis des Materials, wurde das Gemisch[2] von der Ketonbase (V) und der Alkoholbase (VI) ohne Trennung angewendet. Die Bleikathode wurde nach Tafel[2] sorgfältig präpariert. 8 gr. des Basengemisches, gelöst in 160 c.c. 25% Schwefelsäure, erfüllte das Kathodenraum, und die Anodenflüssigkeit bestand aus 900 c.c. 10% H_2SO_4. Stromskonzentration 9–9.5 amp. / 100 c.c. Dauer 3 Stunden.

Die Kathodenflüssigkeit wurde dann mit 160 c.c. 20% NaOH alkalisiert. Der Niederschlag wurde in wenig Salzsäure gelöst und wieder mit Natronlauge gefällt. Die Fällung wurde mit viel Wasser gewaschen und dann aus Aceton unkrystallisiert. Ausbeute 1.2 gr. Schmp. 149° (Keine Erniederung in der Mischprobe mit der Substanz, gewonnen in II). Diazoreaktion noch erkennbar in 1 : 2,000,000 Verdünnung.

Das Jodmethylat schmolz bei 267° (aus Wasser), ebenso die Mischprobe mit demjenigen, gewonnen durch Clemmensenschen Methode.

Aus dem alkalilöslichen Teil, wurden 2.2 gr. reiner Demethoxydihydrosinomeninol (VI) zurückgewonnen, nebst 0.5 gr. Kristalle von dem Gemisch von den beiden Basen. Gesamte Ausbeute 3.9 gr. d.h. etwa 50%.

Da die Alkoholbase, wie man aus der Tabelle 1 ersehen kann, sehr schwer nach Tafel reducierbar ist, muss zweifellos die gesammte Ausbeute an Desoxo-demethoxy-dihydrosinomenin aus der Ketonbase entstanden haben.

(1) *Ber.*, **63** (1930), 646.
(2) Siehe die Bemerkung zu Tabelle 1.
(3) *Ber.*, **33** (1900), 2226.

Bei der Prüfung der Diazoreaktion an einzelnen Krystallisationen ergab sich dass es nie eine Fraktion gab, in der die Reaktion abgeschwächt ist.

II. Ueberführung von Demethoxy-dihydrosinomenin (V; d-Dihydrothebainon) ins Desoxo-demethoxy-dihydro-sinomenin (II; d-β-Tetra-hydrodesoxycodein). Diese Umwandlung geschah ganz in derselben Weise wie M. Freund[1] in der Bereitung von β-Tetrahydro-desoxy-codein aus Codein angegeben haben. 10 gr. wohl getrockneter Demethoxy-dihydro-sinomenin wurden portionsweise in das eisgekühlte Gemisch von 11 gr. Phosphorpentachlorid und 60 c.c. Chloroform eingetragen. Nach dem Stehenlassen übernachts, wurde das Hydrochlorid der Base mit viel Aether als öliger Niederschlag gefällt. Der letztere wurde mit viel (150 c.c.) gesättigter Sodalösung auf dem Wasserbad digeriert. Das Dichlorid wurde dabei krystallinisch, aber nie rein genug zur Analyse.

Das Dichlorid wurde, daher, ohne weitere Reinigung, der katalytischen Reduktion mit kolloidalem Palladium (aus 0.5 gr. $PdCl_2$+ wenig Gummi arabicum) in essigsauer Lösung unterworfen. Die Aufnahme von Wasserstoff betrug auf etwa 1,000 c.c. in anderthalb Stunden. Die in der üblichen Weise daraus isolierte Base bildete vier=oder sechs=eckige Tafeln, schmolz bei 147–148° und zeigte alle dieselben Eigenschaften mit der, die durch Clemmensensche Reduktion gewonnen worden war. Ausbeute etwa 25%.

Anal. Subst.=7.092; CO_2=19.544; H_2O=5.551 mg. Subst.=7.437 mg.; N_2=0.319 c.c. (15°, 760 mm.) Gef.: C=75.16; H=8.63; N=4.91%. Ber. für $C_{18}H_{25}NO_2$ (287): C=75.26; H=8.71; N=4.88%.

Das Jodmethylat schmolz scharf bei 267–268° (aus Methanol).

III. Des-N-Methyl-desoxo-demethoxy-dihydro-sinomenin. Fünf gramm des Jodmethylates der Base (II) (Schmp. 267° aus Wasser) wurden in 20 c.c. Wasser heiss gelöst und unter Zusatz von 20 c.c. 50% KOH eine halbe Stunde im Glycerin-bad gekocht. Beim Sättigen der abgekühlten und mit Wasser verdünnten Lösung mit Kohlensäure, schied sich ein flockiger Präcipitat, welcher in Alkohol aufgenommen und dann in viel Aether eingegossen wurde. Beim Abdampfen des Aethers blieb ein Syrup, der sich durch Rühren mit Aether krystallisieren liess. Aus Methanol umkrystallisiert, bildete es lange Prismen die beim 147–148° scharf schmolzten. Ausbeute 0.4 gr. d.h. etwa 15% der Theorie. (Formel XII).

Anal. Subst.=4.52; CO_2=12.587; H_2O=3.742 mg. Subst.=5.286 mg.; N_2=0.218 c.c. (15°, 760 mm.) Gef.: C=75.95; H=9.19; N=4.72%. Ber. für $C_{17}H_{27}O_2N$ (301): C=75.75; H=8.97; N=4.65%.

(1) *J. prakt. Chem.*, **101** (1921), 21.

Der stickstofffreie Körper. Da das Jodmethylat der des-Base keine Neigung zur Krystallisation zeigte, wurde es sofort mit Kalilauge abgebaut. Das Jodmethylat, bereitet aus 0.9 gr. der des-Base und 0.8 gr. Jodmethyl, wurde mit 10 c.c. 25% Kalilauge 20 Minuten gelinde gekocht. Das beim Abkühlen erstarrende Öl wurde mit Wasser gewaschen und in Aether aufgenommen. Der gewaschene und getrocknete Aether liess eine krystallinische Masse hinter, die sich aus Methanol in langen, schönen Prismen krystallisieren lassen hat. Schmp. 107 ~ 108° (vorheriges Sintern bei 97~98°). Ausbeute mehr als 50% der Theorie. (Formel XIII).

Anal. Subst.=5.444; CO_2=15.945; H_2O=3.797 mg. Gef.: C=79.88; H=7.75%. Ber. für $C_{17}H_{20}O_2$ (256): C=79.69; H=7.81%. 0.0191 gr. Subst. in 0.1848 gr. Campher. Erniederung 16.4°. Mol. Gew. Gef. 252.

IV. Clemmensensche Reduktion von Sinomenin und seinen Derivaten. Zinc-amalgam wurde nach Clemmensen bereitet. Je 1 gr. der Substanz wurde mit Ueberschuss von diesem Amalgam und 10 c.c. Salzsäure (1 : 1) ein oder zwei Stunden auf dem Wasserbad erhizt. Nach dem Ende der Reduktion, wurde die salzsaure Lösung von dem Amalgam abgegossen und mit Wasser sorgfältig verdünnt, dabei fällt das $ZnCl_2$-Doppelsalz (?) der reducierten Base in syrupöser Form.

Das lelztere wurde in wenig Aceton gelöst und in viel Chloroform eingegossen. Wenn dabei zu viel ungelöste Substanz bleibt, wird die Operation einigermals wiederholt. Die Aceton-Chloroformlösung wurde dann mit verdünntem Ammoniak gründlich geschüttelt und mit Wasser gewaschen. Beim Abdampfen der getrockneten Chloroformlösung bleibt ein Syrup züruck, welcher sich aus Aceton in vier- oder sechseckigen Tafeln krystallisieren läszt. Schmp. 148°. Ausbeute gewöhnlich etwas 30% der Theorie.

Aus der salzsaure Lösung gewinnt man natürlich etwas mehr von dieser Substanz, aber durch die obige Arbeitsweise bekommt man schnell das reinste Examplar.

Die Resultate dieser Reduktion mit verschiedenen Derivaten des Sinomenins sind in der Tabelle 2 zusammengefasst.

Chemisches Laboratorium der
Kitasato Institut, Tokyo.

STUDIES ON THE CONSTITUENTS OF THE VOLATILE OIL FROM THE LEAF OF *CHAMAECYPARIS OBTUSA*, SIEB. ET ZUCC., F. *FORMOSANA*, HAYATA, OR ARISAN-HINOKI. I.

By Kinzo KAFUKU, Tetsuo NOZOE and Chuta HATA.

Received January 9, 1931. Published February 28, 1931.

It was S. Uchida[1] who first studied the oil of *Chamaecyparis obtusa*, Sieb. et Zucc. f. *formosana*, Hayata, or Arisan-Hinoki. His oil, however, consisted of the product of dry distillation of the wood, and he reported to have found *d*-α-pinene and *l*-cadinene in the oil. Nextly, R. Tsuchihashi and S. Tasaki[2] studied the oil obtained by steam distillation of old root-stumps of the same plant, and proved the presence of *d*-α-pinene, *d*-α-terpineol, isoborneol, *d*-cadinene, a dicyclic sesquiterpene alcohol, an acid of the formula $C_9H_{16}O_2$ or $C_9H_{14}O_2$, and a phenolic substance of the formula $C_{10}H_{12}O_2$. Later, N. Hirao[3] examined a similar oil and found camphene, borneol, camphor, and an acid of the formula $C_{10}H_{16}O_2$ aside from those previously mentioned. To this acid Hirao gave the name "chamaenic acid," he also suggested that terpinolene and β-terpineol might probably be present. In all of these cases, the main component of the oil were *d*-α-pinene, *d*-α-terpineol, and cadinene. More recently, S. Uchida[4] published the result of his studies of the oil from the leaves of Japanese Hinoki (*Chamaecyparis obtusa*, Sieb. et Zucc.) and the following constituents are stated to have been found: — *d*-α-pinene; *d*-limonene; borneol, bornyl acetate; bornyl nonylate; a tricyclic sesquiterpene with a little cadinene; a dicyclic sesquiterpene alcohol; a tetracyclic diterpene; a new acid $C_{16}H_{24}O_2$. The last substance was named "hinokic acid" by the author. In quantity, *d*-α-pinene, *l*-limonene, and bornyl acetate predominated.

So far as the present authors are aware, however, there has been no report concerning the constituents of Formosa Hinoki leaf oil, and the authors took to the study of this oil which turned out to be quite different in composition from those cited above.

The main constituents of the acidic part was an unsaturated fatty acid possessing the physical properties resembling those of the acid described by Tsuchihashi and Tasaki (loc. cit.), but the results of analyses, molecular

(1) *J. Soc. Chem. Ind. Japan*, **19** (1916), 611.
(2) *Report of Gov. Research Inst. Formosa*, **1** (1920).
(3) *J. Chem. Soc. Japan*, **47** (1926), 666, 743.
(4) *J. Soc. Chem. Ind. Japan*, **31** (1928), 650.

weight determinations, and the molecular refraction corresponded to $C_{10}H_{16}O_2$ instead of $C_9H_{16}O_2$ or $C_9H_{14}O_2$. Chamaenic acid described by Hirao (loc. cit.) could not be found in our oil. The following table shows the data as regards these acids.

Table 1.

	Tsuchihashi-Tasaki	Hirao	Kafuku-Nozoe-Hata
Origin	wood	wood	leaf
B. p.	134°–140°/5mm.	130°–134°/6mm.	133°–135°/6mm.
Density	0.9507 $(^{24}/_{4})$	1.0092 $(^{20}/_{4})$	0.9544 $(^{20}/_{4})$
n_D	1.4784 (24)	1.5271 (20)	1.4732 (20)
Formula	$C_9H_{16}O_2$	$C_{10}H_{16}O_2$	$C_{10}H_{16}O_2$
Mol. refr.	—	51.10	49.40
Br-absorption	—	2 Br.	2 Br.
Coloration with $FeCl_3$	—	deep red	deep red

see errata V. 6, P. 341

Our acid, which perhaps is an aliphatic acid of the terpene series, gave a deep red coloration with a drop of dilute alcoholic solution of ferric chloride, precisely as is stated by Hirao in case of chamaenic acid (loc. cit.)—and moreover, it deposited a minute quantity of dark red crystals; but, as regards the exact nature of this acid, we must leave it for the future study.

see errata V. 6, P. 341

On fractionation of the acid-free oil, the fraction boiling between 165° and 175° showed a density too low for an ordinary terpene and moreover it was very unstable and liable to oxidize on exposure to the air and ready to undergo polymerization. With a view that it might contain some new terpenes possessing definite properties, we carefully fractionated it repeatedly over metallic sodium under partial vacua and obtained at last a hydrocarbon of a characteristic odor with following constants: Boiling point=86°—88° under 50 mm.; $d_4^{25}=0.8228$; $n_D^{25}=1.4686$; rotatory power$_D^{25}$ =about+35°.

From considerations of its molecular refraction, its bromine number, and its non-reducibility by sodium and alcohol, it becomes evident that the hydrocarbon is neither a menthene nor a mixture of cyclic and chain terpenes, but a hitherto unknown new terpene of monocyclic nature. The authors wish to propose the name "*chamene*" to this new terpene, which, so far as the authors are aware, has the lowest density among all naturally occurring monocyclic terpenes, as shown in Table 2.

Table 2.

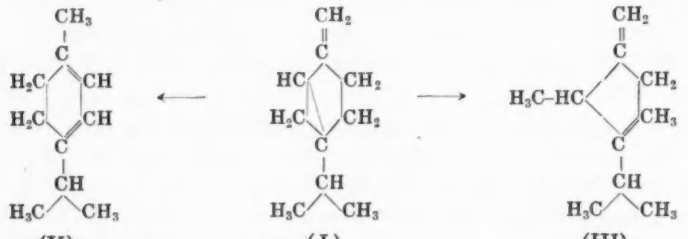
	B. p.	d_{20}	n_D^{20}	M.R.	M.R. as $C_{10}H_{16}$
Limonene	175°–176°	0.845	1.4746	45.24	45.24
Terpinolene	184°–188°	0.857	—	—	—
Terpinene	179°–181°	0.846	1.480	45.65	—
Phellandrene	170°–176°	0.845	1.4788	45.63	—
Sylvestrene	175°–176°	0.848	1.4753	45.23	—
Chamene	168°–170°	0.827	1.472	46.0	—

Chamene is easily oxidized on being kept in the air, thereby changing into a viscous oxygenous compound of higher density, and if shaken with an amount of dilute sulphuric acid it loses its optical activity and changes into another new terpene, to which we propose the name "*isochamene.*" Isochamene is fairly more stable than chamene but the physical properties remain almost unchanged, and it is not yet fully explained whether this change is due to isomerization or racemization. If alcoholic potash is used instead of dilute sulphuric acid, then an inactive diterpene "diisochamene" results.

Semmler,[1] on treating sabinene with concentrated formic acid at -20°C., obtained besides α-terpinene and formic ester of origanol (terpinenol-4), a hydrocarbon $C_{10}H_{16}$ with the following properties: Boiling point=50°—54° under 10mm., 169°—173° under 760mm.; d^{20}=0.829—0.831; n_D^{20}=1.470; α_D=+13°—(+24°).

see errata Y. 6, P. 341

From the fact that this hydrocarbon showed a very low density and that its optical activity did not enfeeble even when it was boiled with an acid, and from the supposition that a semicyclic double linking is less influenced by acids than the cyclopropane ring, he assumed this hydrocarbon to be a derivative of cyclopentadiene of the formula (3) given below, but as to its chemical behaviors nothing is described in his paper:



(II) α-Terpinene (I) Sabinene (III)

(1) *Ber.*, **39** (1906) 4414.

It is not difficult to consider that this hydrocarbon and chamene or isochamene to be in close connection,—although may or may not be the same substance,—as Semmler's formula is in accordance with such properties of chamene as the tendency to polymerize, isomerize or oxidize by itself. But it is absolutely necessary to determine at first whether this hydrocarbon does actually possess a pentamethylene ring, or not; and experiments are being carried out in this direction.

Fractions distilling below 158° had a fairly low specific gravity and were still unstable even though sabinene and chamene had been removed by repeated fractionations, which fact led us to test for the presence of *α*-thujene and *α*-pinene. For this purpose we oxidized this fraction with dilute potassium permanganate and ketonic acids formed thereby were isolated as their semicarbazones. After repeated fractional crystallizations from dilute alcohol we succeeded in separating them into two parts, the one of which represented the semicarbazone of pinonic acid melting at 206°—207° while the other that of thujaketonic acid,[1] melting with decomposition at 180.5°—181.5°. Thus, it is most probable that *α*-thujene is contained in the oil, although any further identification could not be made.

An intermediate portion distilling between the terpene and terpene alcohol fractions possessed a characteristic pleasant odour reminding esters, so that it was saponified and a free alcohol of the formula $C_8H_{16}O$ was obtained. This alcohol represented an octenol, secondary in nature, but quite different from ordinary methyl heptenol. It had a peculiar musty odour and on oxidation with Beckmann's mixtures, it gave a product other than the ordinary methyl heptenone. The exact nature of this alcohol, however, could not be determined because of the small quantity available.

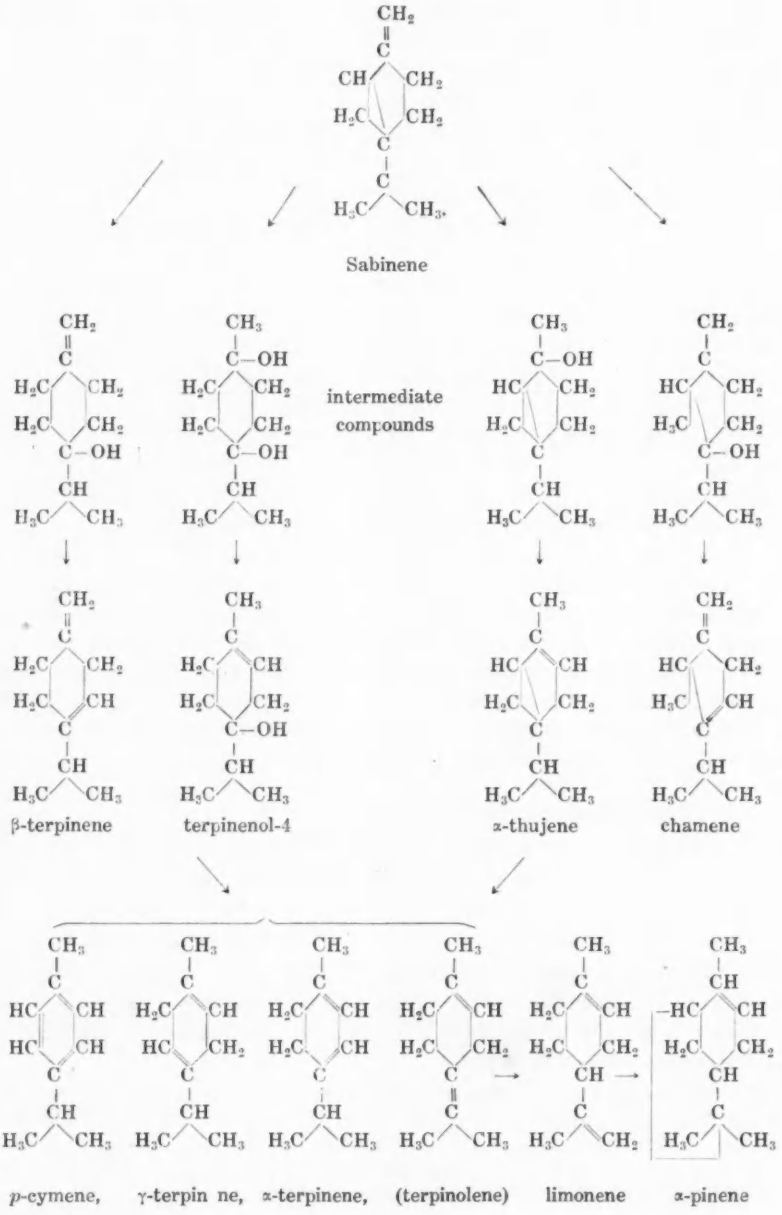
To summarize our results briefly:

1. The acidic portion which amounted to about 0.85% of the whole oil, consisted mainly of an unsaturated fatty acid of the formula $C_{10}H_{16}O_2$, and hinokic acid, $C_{16}H_{24}O_2$, melting at 165°—166°, together with a small quantity of an acid, probably caproic acid, and a trace of phenolic substances.

2. The terpene part occupied about 34% of the oil, of which about 50% consisted of *d*-sabinene, and 20—30% of a new terpene "*chamene*," the remainder represented *d*-*α*-pinene, *p*-cymene, *α*-terpinene, *γ*-terpinene, *α*-thujene, and a trace of dipentene.

3. The constitutional formula for chamene was partly deduced, but not yet fully established.

(1) Wallach (*Ber.*, **30**, 426), Thuja-ketonic Acid m.p.=182°–183°.
Semmler (*Ber.*, **35**, 552), Thuja-ketonic Acid m.p.=198.5°.


Sabinene
intermediate compounds
β-terpinene
terpinenol-4
α-thujene
chamene
p-cymene,
γ-terpin ne,
α-terpinene,
(terpinolene)
limonene
α-pinene

4. The terpene alcohol fraction occupied about 11.6% of the original oil, which consisted mainly of *d*-terpinenol—4. Besides, there were found a small amount of a laevo-rotatory alcohol of the formula $C_8H_{16}O$ and *l*-linalool, both for the most part in form of esters, and in addition to these a trace of borneol was found to present.

N. B. It is of interest that the chief constituents of the leaf oil, *d*-sabinene, *d*-chamene, and *d*-terpinenol-4, have never been found in the oils from root or wood, while *d*-α-pinene, dipentene, and α-terpineol which form the main part of the latter oils are to be found in the former oil either in very small quantities or not at all. Moreover, it seems peculiar, that almost all the constituents found in this oil are to some extent related to sabinene as may be seen from the scheme in the foregoing page.

Experimental.

The oil used for these experiments was obtained at Arisan (Mt. Ari) by steam distillation of the fresh leaves of "benihi"-cypress or *Chamaecyparis Obtusa*, Sieb. et Zucc. f. *formosana*, Hay.; the yield amounting to 0.3% of the weight of live leaves. The oil had a characteristic pleasant odour and was of slightly yellow colour which gradually changed into deep red on standing. The properties of the oil were as follows: $d^{25}=0.8988$; $n_D^{25}=1.4878$; $\alpha_D^{25}=-5.83°$; Acid value=0.96; Ester value=12.63; Do. after acetylation=54.81.

The Acidic Part. The acid part was extracted from the oil by shaking with 5% caustic potash, and it was then regenerated from the aqueous solution in the usual way by means of carbon dioxide and dilute sulphuric acid. From 5 kg. of oil 12 gr. of the acidic part and 1.5 gr. of phenolic part were obtained.

This acidic mixture was fractionally distilled in vacuo three times successively, and from the fractions we could identify the following constituents:

i) *An Unsaturated Fatty Acid*, $C_{10}H_{16}O_2$. This formed the main fraction which had the following constants: B.p.=133°—135°; $d_4^{20}=0.9544$; $n_D^{20}=1.4732$; $\alpha_D=0°$; M.R.=49.40 as $C_{10}H_{16}O_2$, calculated value 48.99.

Anal. Subst.=0.1365; $CO_2=0.3558$; $H_2O=0.1233$ gr. Found: C=71.08; H=10.03%. Calc. for $C_{10}H_{16}O_2$: C=70.58; H=10.58%. Calc. for $C_{10}H_{18}O_2$: C=71.42; H=9.50%.

0.0999 gr. substance in carbon tetrachloride at 0°C. absorbed 0.0948 gr. bromine. Calculated for $C_{10}H_{16}O_2Br_2$: Br=0.0950 gr.

Molecular weight. 0.2067 gr. acid required 12.65 c.c. of normal caustic soda (N=0.969) for neutralization, corresponding to a molecular w ight of 168.6. $C_{10}H_{16}O_2=168.2$. 2.80 mg. of the silver salt gave 1.07 mg. silver, corresponding to a molecular weight of 168.4.

Neither an acid amide nor an anilide could be obtained in the crystalline form.

The solution of this acid gave an intense red coloration on shaking with a few drops of ferric chloride solution and deposited a small amount of dark red crystalline precipitate on standing, but the nature of this precipitate, however, has not been studied further.

ii) *Hinokic Acid.* The fraction boiling above 150° under 2 mm. pressure, solidified on standing and after recrystallization from dilute alcohol melted at 165°—166°. This acid is in all probability identical with Uchida's hinokic acid.

iii) Besides, there was a trace of lower fatty acid, which judging from the results of analyses of its silver salt, seemed likely to be caproic acid.

iv) Phenols, with lower boiling point, gave reddish violet coloration to alcoholic ferric chloride, while the higher ones, a deep bluish green on the same treatment, but on account of the small quantity we could not identify any of the individual phenols.

The Neutral Part. A preliminary examination has shown that the oil did not contain any noticeable quantity of aldehydes or ketones (shaking with concentrated sodium bisulphite solution), and moreover, that it was rather unstable to the action of the acid, so we fractionated the oil directly without any treatment beforehand.

2500 c.c. of the oil was fractionated carefully under reduced pressures, and after four consecutive fractionations the whole was divided into the following six sections:

see errata V. 61, P. 341

Table 3.

(A)	40° – 80°/50 mm.	1362 gr.	34.1% (Terpenes)
(B)	80°—120°/50 mm.	456 gr.	11.4% (Terpene alcohols)
(C)	120°—140°/50 mm.	1607 gr.	40.2% (Sesquiterpenes)
(D)	140°—160°/50 mm.	394 gr.	9.6% (Sesquiterpene alcohols)
(E)	160°—180°/50 mm.	52 gr.	1.8% (Diterpenes)
(F)	The residue	16 gr.	0.4%

In all of the fractional distillations the authors used Widmer's fractionating column.

The Terpenes. The fraction (A) in the foregoing table was further fractionated over metallic sodium under 50 mm. pressure and separated into the following eleven fractions as shown below:

Table 4.

No.	B.p./50 mm.	Yield	d_4^{22}	n_D^{22}	α_D^{22}
1	76°— 78°	53 gr.	0.842	1.4651	+30.4°
2	78°— 80°	131	0.839	1.4662	+40.9°
3	80°— 82°	171	0.835	1.4673	+48.3°
4	82°— 84°	128	0.830	1.4685	+48.7°
5	84°— 86°	76	0.830	1.4698	+42.3°
6	86°— 88°	44	0.829	1.4705	+35.2°
7	88°— 90°	12	0.831	1.4712	+27.5°
8	90°— 92°	40	0.833	1.4726	+20.4°
9	92°— 94°	50	0.837	1.4746	+13.1°
10	94°— 98°	67	0.847	1.4773	+ 5.5°
11	98°—106°	5	0.870	1.4740	+ 3.0°

The New Terpene "Chamene." As the fractions (3) to (7) had a very low specific gravity, and were liable to deposit a viscous liquid (not water) on exposure to the air, we studied these fractions first of all. These were once again repeatedly and systematically fractionated over metallic sodium and at last we could obtain a rather pure sample with the following constants: B.p. = 86°—88° under 50 mm., 168°—170° under 760 mm.; $d_4^{25} = 0.8228$; $n_D^{25} = 1.4686$; $\alpha_D = +35.0°$; M. R. = 46.00, calculated as $C_{10}H_{16}$ $\overline{=}_2$ =45.2.

As chamene was ready to oxidize in the air, the authors experienced difficulty in getting good results in analyses.

0.2745 gr. substance absorbed 0.7033 gr. bromine, the amount calculated for $C_{10}H_{16}Br_2$ being 0.6443 gr.

The hydrochloride was obtained by saturating the ethereal solution of the hydrocarbon with dry hydrogen chloride for two days in the cold. The product was a liquid which boiled at 80°—90° under 11 mm. pressure with a density 1.0196 at 25°C., and a refractive index 1.4783 at the same temperature. The molecular refraction found was 58.09 as $C_{10}H_{18}Cl_2$ or 50.58 as $C_{10}H_{17}Cl$, while those calculated were 55.91 as $C_{10}H_{18}Cl_2$ ($\models$ =0) and 50.58 as $C_{10}H_{17}Cl$ ($\models$ =1).

Attempts to reduce the hydrocarbon itself or this hydrochloride with sodium and alcohol were not effective; also all efforts to get characteristic crystalline substance proved unsuccessful.

Chamene, especially in the pure state, was very unstable and liable to change into a viscous liquid insoluble in the original terpene which seemed

likely to be a peroxide. As for the exact nature of the products of oxidation it should remain to be reported until the next opportunity.

Isomerisation of chamene was carried out by shaking 20 gr. of chamene with 20 c.c. of dilute sulphuric acid (1:3) for two hours at room temperatures, when its optical activity all but disappeared and a new isomeric terpene was obtained, which was thoroughly washed with water, dried over anhydrous sodium sulphate, and then rectified in vacuo. This terpene, to which we suggest the name "*isochamene*," was found to possess the following constants: B.p.=88°–90° under 50 mm.; $d_4^{25}=0.8222$; $n_D^{25}=1.4726$; $\alpha_D^{25}=-0.27°$; M.R.=46.42, calculated as $C_{10}H_{16}\overline{=}_2=45.2$.

Anal. Subst.=0.1088; $CO_2=0.3475$; $H_2O=0.1123$ gr. Found: C=87.11; H=11.46%. Calc. for $C_{10}H_{16}$: C=88.23; H=11.77%.

Contrary to chamene, isochamene was found to be fairly more stable than chamene against the action of the air.

Polymerization of isochamene to its dimeride ensued when alcoholic sulphuric acid (1:1) was used instead of the aqueous in the experiment described above; the rotatory power being destroyed almost to nothing in half an hour with appreciable evolution of heat. The product represented a mixture of a diterpene with a little isochamene, which was rectified in the usual manner and the diterpene with the following properties was obtained: B.p. = 155°–156° under 4 mm.; $d_4^{20}=0.9150$; $n_D^{20}=1.5134$; $\alpha_D^{20}=-0.7°$; M.R.=89.40, calculated as $C_{20}H_{32}\overline{=}_3=88.76$.

The name "*diisochamene*" is given by the authors to this new diterpene as it was obtained by the condensation of two molecules of isochamene.

To a well-cooled mixture of a benzol solution of isochamene and a calculated amount of sodium nitrite solution under stirring, glacial acetic acid was added drop by drop, when the solution assumed a blue colour at first which gradually turned into yellow. No crystal formation set in before the solution was warmed once again to about 50° when it suddenly deposited a quantity of colourless needles which after recrystallization from dilute alcohol, melted at 154°–155°. Strangely enough, this crystal was proved to be identical with α-terpinene nitrosite by observing the mixed melting point with an authentic specimen of the same. Whether this nitrosite resulted from by-mixed terpinene really existent in the isochamene fraction or from an intramolecular rearrangement of isochamene nitrosite, is not clear, but from consideration of the feature and quantity of crystal formation, the latter course seems the more probable.

Chamene dissolved in acetic anhydride, if treated with a drop of concentrated sulphuric acid, a deep red coloration is produced.

The total amount of chamene in the oil perhaps amounted to 20—30% although the final product in the pure condition was rather small in quantity.

The Terpenes boiling lower than Chamene. The fractions of lower boiling terpenes—No. 1 to No. 6 were further fractionated under ordinary pressures over metallic sodium and they were divided into the following eleven fractions taking into consideration their optical activities:—

Table 5.

No.	α_D^{18}	B.p./760 mm.	n_D^{18}	d_4^{19}	Yield	M.R.
1	− 4°—+0°	153.0°—155.0°	1.4628	0.8463	14 gr.	44.6
2	+ 0°—+5°	155.0°—155.5°	1.4642	0.8475	20	44.3
3	+ 5°—+10°	155.5°—156.0°	1.4647	0.8477	13	44.3
4	+10°—+15°	156.0°—156.5°	1.4651	0.8477	21	44.4
5	+15°—+20°	156.5°—157·0°	1.4655	0.8474	29	44.4
6	+20°—+32°	157.0°—157.5°	1.4661	0.8469	24	44.5
7	+32°—+40°	157.5°—158.0°	1.4665	0.8462	18	44.6
8	+40°—+50°	158.0°—159.0°	1.4669	0.8453	35	44.6
9	+50°—+60°	159.0°—160.0°	1.4677	0.8435	30	44.8
10	+60°—+62°	160.0°—161.0°	1.4680	0.8425	15	44.9
11	+62°—+66°	161.0°—162.0°	1.4690	0·8420	150	45.0

From these fractions we could identify *α*-pinene, *α*-thujene, and *d*-sabinene.

α-Pinene. The presence of *α*-pinene was proved by preparing nitroso-chloride, nitrolbenzylamine, nitrolpiperidine, and pinonic acid melting at 106°—107°, 121°—122.5°, 118°—119°, and 206.5°—207 respectively. see errata V. 6, P. 341

d-Sabinene. Fraction (11) represented nearly pure sabinene, whose presence being confirmed by preparing the sparingly soluble sodium salt of sabinic acid, and the free acid melting at 58°—58.5° from the products of oxidation of the fraction with alkaline permanganate. Besides, we obtained sabina ketone and its semicarbazone (m.p. 141°—142°). It should be mentioned that our sabinene was found to possess the highest optical activity. The hitherto observed highest data being + 68.54°(1) while the authors' sabinene after careful rectifications showed the following constants: B.p.=161°—163°; $d_4^{17.5}$=0.8442; $n_D^{17.5}$=1.4695; $\alpha_D^{17.5}$=+72.94°; $[\alpha]_D^{17.5}$=+86.4°; M.R.=44.90, calc. as $C_{10}H_{16}$=43.51.

(1) Ber. von Schimmel & Co. – Gildemeister u. Hoffmann, "Die Ätherischen Öle," Vol. 1, p. 356.

α-Thujene. A well-cooled mixture of the fractions No. 3 to No. 6 (45 gr.) was oxidized by means of alkaline permanganate solution, and the resulting oxidized products were treated in the usual manner and obtained 30 gr. of acid. This was extracted with ether and the extract was neutralized with sodium hydroxide. On evaporation 3.5 gr. of sodium sabinate separated out as crystals while from the filtrate 22 gr. of other acids were recovered. These gave on treatment with semicarbazide hydrochloride, about 12 gr. of a crystalline body melting at 190°—198°, seemingly a mixture of more than two semicarbazones. Thus, it was fractionally recrystallized from dilute alcohol and at last we obtained two different products, the one melting at 201°—203° and the other at 184°—186°. These were further fractionated in the same medium eight consecutive times and were differentiated into (a) the more difficultly soluble prismatic crystals—pinonic acid semicarbazone m.p. 206°—207°, and (b) the more easily soluble thin needle crystals melting with decomposition at 181°—181.5°. This latter melting point coincides with that of α-tanaceto-keto-carboxylic acid semicarbazone,[1] but whether it be such or not is not clear.

Anal. Subst. = 3.61 mg.; N_2 = 0.579 c.c. (30°, 759 mm.) Found: N = 16.95%. Calc. for $C_{11}H_{19}O_3N_3$: N = 17.4%.

The Higher Boiling Terpenes. The fractions (8), (9), (10), and (11), were further fractionated over metallic sodium into the following five fractions:

Table 6.

	B.p./760 mm.	Yield	n_D^{22}	d_4^{22}	α_D^{22}
1)	168°—172°	84 gr.	1.4710	0.8300	+30.0°
2)	172°—175°	16	1.4735	0.8354	+16.6°
3)	175°—178°	44	1.4759	0.8418	+ 8.5°
4)	178°—181°	45	1.4782	0.8471	+ 3.5°
5)	181°—	8	1.4832	0.8545	+ 1.1°

In the above, 1) consisted mainly of chamene, while 3) and 4) contained *p*-cymene, α-terpinene, γ-terpinene and dipentene. The first of these, *p*-cymene, was isolated after repeated treatments with dilute permanganate solution as a mobile, highly refracting liquid of the characteristic smell, from which on oxidation with a more concentrated solution of potassium

(1) Wallach, *Ber.*, **30**, 426.

permanganate, crystals of *p*-oxy-isopropyl-benzoic acid[1] (m.p. 115°—Mischproben) was obtained. The presence of *α*-, and *γ*-terpinenes was proved by preparing *αα'*-dioxy-*α*-methyl-*α'*-isopropyl adipic acid[2] (m.p. 188°—189°—Mischproben) and *γ*-terpinene erythrite (m.p. 236°—238°—Mischproben) respectively. Dipentene was found in small quantity in 4) from which the tetrabromide could be prepared in the ordinary way.

The presence of Δ_3-, and Δ_4-carenes, *α*-, and *β*-phellandrenes was suspected and tests in these directions were made but without success.

The Terpene Alcohols. The fraction (B), which consisted mainly of terpene alcohols, was submitted to a careful and systematic fractionation under reduced pressures (at first under 12 mm., and finally under 50 mm. pressure), and ultimately it was divided into the following twelve fractions:

Table 7.

	B.p./50 mm.	Yield	d_4^{20}	n_D^{20}	α_D^{20}	Ester value
(1)	up to 105°	11 gr.	0.853	1.476	+ 2.5°	—
(2)	105°—112°	3	—	1.465	+ 3.8°	—
(3)	112°—115°	2	0.884	1.458	+ 4.9°	78.5
(4)	115°—118°	7	0.899	1.464	+ 9.5°	44.2
(5)	118°—121°	17	0.907	1.468	+13.5°	—
(6)	121°—124°	78	0.931	1.475	+20.1°	29.1
(7)	124°—127°	22	0.930	1.472	+19.2°	51.8
(8)	127°—130°	12	0.928	1.468	+14.5°	—
(9)	130°—133°	13	0.926	1.466	+ 4.3°	157.2°
(10)	133°—136°	5	—	1.467	+ 0.5°	157.8
(11)	136°—140°	6	0.932	1.477	- 12.5°	109.0
(12)	140°—145°	7	0.934	1.481	−25.6°	80.5

With these fractions the following identifications were made:

i) *An Octenol $C_8H_{16}O$ and its Ester.* The fractions (2) and (3) had a characteristic pleasant odour reminding the presence of an ester, therefore we mixed the fractions (1) to (4) and saponified the mixture by heating with alcoholic potash for two hours. The free alcohol thus obtained was purified by distillation in vacuo, the constants of which are: $d_4^{20}=0.8454$; $n_D^{20}=1.4441$; $\alpha_D^{20}=-10.62$.

Anal. Subst. = 0.1189; CO_2 = 0.3290; H_2O = 0.1298 gr. Found: C = 75. 8; H = 12.12%. Calc. for $C_8H_{16}O$: C = 75.00; H = 12.50%.

(1) Wallach, *Ann.*, **264** (1891), 10.
(2) Wallach, *Ann.*, **362** (1908), 297.

The purified alcohol had a peculiar not-unpleasant odour but reminding of mouldy cellar, did react with phthalic anhydride not at 100°C., but at 130° with formation of an ester-acid. The physical constants of this alcohol almost coincided with those of methyl heptenol, but these two differed distinctly in their odour as well as their behaviour towards Beckmann's chromic acid mixture,—the former in not giving the ordinary methyl heptenone while the latter did. The attempt to prepare crystalline derivatives from the alcohol were altogether futile.

ii) *d-Δ_1-Terpinenol-4.* The fractions (5) to (7) represented a free terpene alcohol with a little ester, so they were saponified to get rid of the latter, and then distilled, when, it was found that the main fraction boiled very constantly at 122°—123° under 50 mm. pressure. The properties of the main distillate are as follows: $d_4^{14}=0.9410$; $n_D^{14}=1.4806$; $\alpha_D^{14}=+23.58°$; M.R.=45.9°, calc. as $C_{10}H_{15}OH\,{}^{\Delta_1}_{\Delta_1}$ =45.04.

These constants agree fairly well with those of *d-Δ_1*-terpinenol-4 so the following derivatives were prepared for the identification. *Nitrosochloride.* The nitrosochloride was prepared just in the same way as in the case of pinene, and was found to melt at 109°—110°. The nitrolpiperidin derived from this melted after purifications at 178°—179°, and showed no depression of the melting point on admixture with pure *β*-nitrolpiperidin of *i-Δ_1*-terpinenol-4 (m.p. 181°). *1, 2, 4-Trioxyterpane.* The alcohol, on treatment with an ice-cold, dilute, alkaline permanganate solution, gave 1, 2, 4-trioxyterpane[1] which melted after recrystallization from water at 115°—116° (with a molecule of water of crystallization) and after being dried at 80° in vacuo at 124°—125°.

iii) *Borneol.* In course of the above described experiment, during the steam distillation of the oxidized products, a small quantity of needle-like crystal was observed to separate out in the colder part of the receiver which on examination was found to possess an unmistakable odour of borneol.

iv) *l-Linalool and its Ester.* The fractions (9) and (10) consisted of esters of very pleasant smell which after saponification and subsequent extraction and distillation gave an alcohol having the characteristic odour of linalool with the following constants: B.p.=116°—118° under 50 mm.; $d_4^{20}=0.8695$; $n_D^{20}=1.4648$; $\alpha_D=-14.28°$.

The alcohol was identified as linalool by obtaining the phenyl urethane melting at 60°—63° whose melting point did not lower on admixture with a known sample of linalool phenyl urethane from 'Ho'-oil. Besides, it gave

(1) Wallach, *Ann.*, **356** (1907), 215; also K. Nagai, Investigation of Shogyu- and Yuju-oils (Monopoly Eureau, Government of Formosa, 1914).

rise to an unmistakable odour of citral on treatment with Beckmann's chromic mixture.

From the caustic residue of the saponification, the acidic constituents were recovered in the usual manner. The recovered acid possessed a smell more like caproic acid, but the analysis of the silver salt, however, showed that the greater part was acetic acid, viz.:—

4.82 mg. substance gave 3.04 mg. silver. Found: Ag=63.1%. Calc. for CH_3CO_2Ag: Ag=64.7%.

It follows that linalool existed in the oil chiefly as acetate and a fraction as an ester of higher fatty acid.

Attempts to prove the presence of α-terpineol as its phenyl urethane or its nitrosochloride did not succeed.

Department of Industry,
Government Research Institute of Formosa,
Taihoku, Formosa.

DISPERSOIDOLOGICAL STUDY OF SILVER SALTS IN AQUEOUS ETHYL ALCOHOL, ACETONE AND PROPIONE SOLUTIONS. I.

By Shinjiro ISHII.

Received January 12, 1931. Published February 28, 1931.

On the Complex[1] Solubility and on the Dispergation of an AgI-Precipitate in Aqueous Ethyl Alcohol and Acetone Solutions of KI.

Historical Introduction and Subject of Investigations. The colloidal synthesis of silver salts which are practically insoluble in an aqueous dispersion medium, was the subject of the classical investigations of

(1) By "complex solubility" P.P. von Weimarn designates the solubility of substance AB in solutions of substance AX or BY, with which AB forms complex molecules; the complex molecules become decomposed on the dilution of the solutions by the dispersion medium. In these cases of dissolution, crystals of substance AB are the solid phase (saturating substance).

A. Lottermoser[1]; who also established that e.g. for the cases of dispergation of an AgI-precipitate in *aqueous* KI solutions of progressively increasing concentrations,[2] the dispergation curves have a maximum point (see Curve A, Fig. 2).

The stability of colloidal solutions of silver salts is explained by Lottermoser (l.c.) by the adsorption of ions; owing to this adsorption the disperse particles acquire electrical charges which hinder coagulation.

P.P. von Weimarn[3] ascribes the causes of stability of these colloidal solutions to kinetic processes taking place on the surfaces of the disperse particles and in the dispersion medium; these processes are closely connected with the formation of complex molecules (e.g. AgI, KI).

On the ground of his investigations embracing the colloidal synthesis in mixtures of alcohols and water, of various salts (amongst them of AgI, AgBr, AgCl, silver-citrate and silver-tartrate) P.P. von Weimarn[4] had arrived at a series of conclusions, of these the two following are of special importance for the present investigations.

(1) Ability for complex-formation increases with decrease in the dielectric constant of the dispersion medium. For instance, in the aqueous ethyl alcohol solutions, the dielectric constant decreases with increase of the concentration of alcohol; therefore, with a certain[5] *constant* concentration of substance AX (or BY) in the solution, owing to increase in the complex-formation, the complex solubility of substance AB increases simultaneously with increase of the concentration of alcohol (e.g. $BaSO_4$ in an alcoholic-aqueous BaI_2 solution; AgI in an alcoholic-aqueous KI solution, etc.). These correlations are represented schematically in Fig. 1.

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(1) Lottermoser, *J. prakt. Chem.*, **72–73** (1905), 39 and 374; *Koll.-Zeitschr.*, **1** (1906), 11; *Z. physik. Chem.*, **60** (1907), 451; *Koll.-Zeitschr.*, **2** (1907), Suppl. I, IV; *Z. physik. Chem.*, **62** (1908), 359; *Koll.-Zeitschr.*, **3** (1908), 31; *Z. physik. Chem.*, **70** (1910), 239; *Koll.-Zeitschr.*, **5** (1909), 78; *Koll.-Zeitschr.*, **36** Erg. (1925), 230; *Collegium* (1925), 573; *Z. angew. Chem.*, **39** (1926), 347.

(2) Lottermoser, *Z. physik. Chem.*, **62** (1908), 376.

(3) P.P. von Weimarn, *J. Russ. Chem. Soc.*, **40** (1908), 1785; *Koll.-Zeitschr.*, **4** (1909), 123; "Kolloides und kristalloides Lösen und Niederschlagen," **2** (1921), Kyoto.

(4) P. P. von Weimarn, *News of the Ural Mining Institute*, **1** (1918–1919), Part III, 38; *Koll.-Zeitschr.*, **28** (1921), 99; **32** (1923), 147. For more details see P.P. von Weimarn's paper referred to in Footnote (1) in the next page.

(5) With weaker concentrations of substance AX or BY, the solubility of substance AB decreases according to the Nernst-Noyes' law. For more details, see P. P. von Weimarn's paper referred to in Footnote (1) in the next page.

(2) Increase in complex-formation and complex solubility of substance AB, when the concentration of alcohol in the alcoholic-aqueous solutions of substance AX (or BY) is increased, has an influence on the stability of colloidal solutions, in narrowing the region of concentrations of substance AX (or BY) within the limits of which the existence of a colloidal solution of substance AB is possible.

These correlations in the case of AgI and KI are shown schematically in Fig. 2.

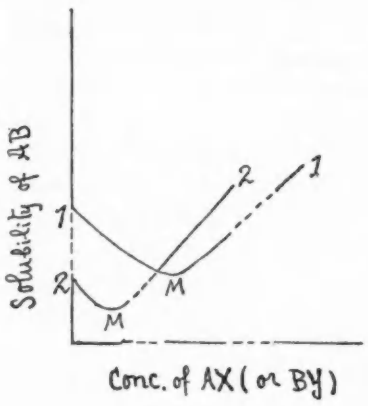
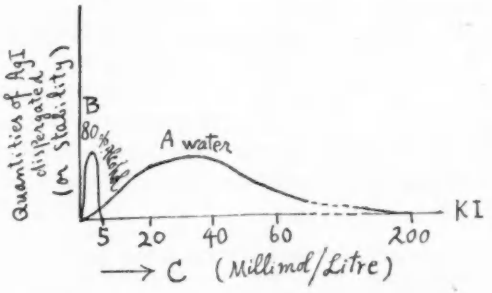


Fig. 1.

(After P.P. von Weimarn. Curve 1 M 1-dispersion medium, water; curve 2 M 2-dipersion medium, e. g. 80% alcohol).

For a clear understanding of the stability of colloidal solutions in presence of complex-formation, P.P. von Weimarn in his recent paper[1] has especially stressed the great importance of quantitative investigations of complex solubility, of adsorption and of other variables. Prof. P.P. von Weimarn was kind enough to suggest to me a quantitative study of the following:



(Curve A, after A. Lottermoser; Curve B, after P. P. von Weimarn.)

Fig. 2.

(1) P.P. von Weimarn, "The influence of solubility, adsorption, complex-formation and solvation, upon the stability of the colloidal state." This paper will appear in the course of this year, in *Kolloidchemische Beihefte.*

1. The dispergation of *precipitates*[1] of different dispersities of AgI, AgBr, AgCl etc. in KI, KBr, KCl etc. ethyl alcoholic aqueous solutions with a progressively increasing concentration of alcohol.

2. The complex solubilities of the same substances.

3. The adsorption of the above-named dispergators.

4. The dispersoidal synthesis of practically insoluble silver salts, in aqueous acetone and propione (diethyl ketone) solutions.

The dielectric constants of acetone and propione are smaller than that of ethyl alcohol (ethyl alcohol, 26.5; acetone, 20.7 and propione, 17.0). Moreover, no investigations have been carried out up to the present upon the colloidal synthesis of practically insoluble silver salts in aqueous acetone and propione solutions.

Up to the present the author has completed the determination of the complex solubility of AgI[2] in aqueous ethyl alcohol and acetone solutions of KI,[3] as well as determining the AgI dispergation curves for these solutions.

Experimental Part.

§ 1. **Complex Solubility, and the Dispergation Curve of AgI in Aqueous Ethyl Alcohol Solution of KI.** An extremely pure AgI-precipitate was prepared for the experiments. It did not show traces of any admixtures ($AgNO_3$ or KI) even when tested by the most sensitive qualitative reactions. In order to reach such a high state of purity the AgI precipitate was washed during ten days with large amounts of water. Further the precipitate was thoroughly washed with ethyl alcohol and dried at 130°C. Micro-and ultramicroscopical investigations of this precipitate showed its polydispersity. A part of the crystals composing the precipitate were of colloidal dimensions, but the degree of their dispersity was not high. The size of other crystals of this AgI-precipitate was above the colloidal; nevertheless they were so small that only seldom could the regularity of their shape be established by microscopic examination under maximum magnification.

(1) Colloidal synthesis of practically insoluble silver salts in statu nascendi (by the double decomposition reaction) was the subject of P.P. von Weimarn's investigations (l.c.). P.P. von Weimarn will continue these researches, especially with aqueous solutions of propyl and butyl alcohols.

(2) On the complex solubility of $BaSO_4$ in alcoholic-aqueous solutions of BaI_2, $BaBr_2$ and $BaCl_2$, see the paper of P.P. von Weimarn and S. Ishii, which will appear in the course of this year, in *Kolloidchemische Beihefte*.

(3) I have also studied crystals of various complex compounds of AgI and KI; certain of these crystals proved to be sensitive to light. The results of this investigation will appear in my paper in the *Reports of the Imperial Industrial Research Institute of Osaka* (1931).

The experiments for the determination of AgI complex solubility in aqueous ethyl alcohol KI solutions were carried out as follows. About 3 gr. of AgI-precipitate and 100 c.c. KI-solution of a definite concentration were placed into a cylindrical glass vessel which after being carefully stoppered, was shaken for half an hour in a shaking machine. After shaking, the vessel containing the disperse system formed, was kept in a thermostat (20°C.) up to the time when complete precipitation of AgI disperse particles took place. The precipitation was regarded as completed when the supernatant solution no longer produced the Tyndall cone (in a dark room, under arc-lamp illumination). This solution, perfectly "optically void," was filtered and about 80 c.c. were taken for the determination of AgI and KI concentrations. After heating the solution in order to eliminate the alcohol, 300 c.c. water were added. The quantity of AgI (precipitated on the addition of water) was determined by gravimetric analysis; and that of KI in the filtrate by volumetric analysis according to Volhard. Complex solubilities, weaker than 1.10^{-4} mol per litre, were determined by tyndallimetry.

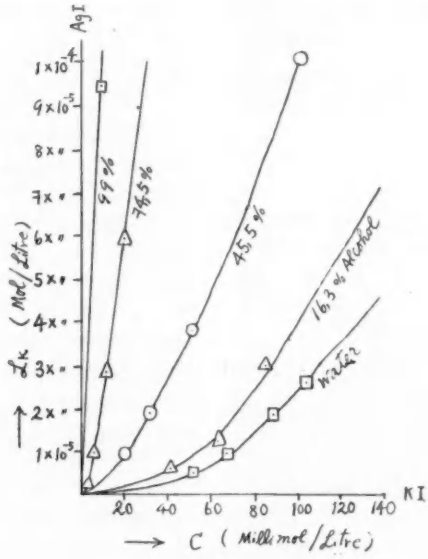


Fig. 3*a*.

In Figs. 3*a* and 3*b* are shown graphically the results obtained by the author (the coordinates for the curves in Fig. 3*a* are L_k, complex solubility in mol-liter, and C, concentration in millimol-liter of KI in the solution; for

the curves in Fig. 3*b* they are $\mathrm{Log}L_k$ and $\sqrt{C}$; the concentration of alcohol is expressed by weight percentage).

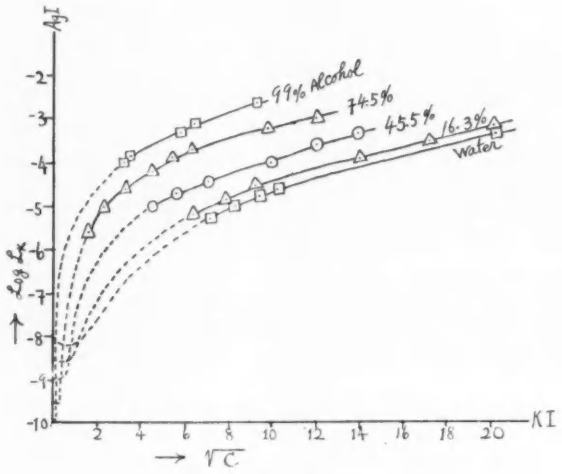


Fig. 3*b*.

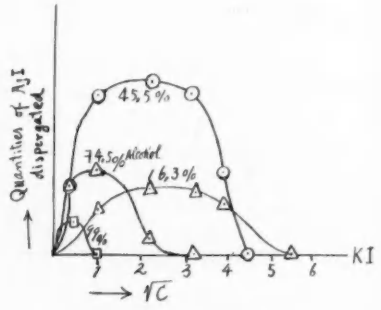


Fig. 4. (After one month)

The experiments on the dispergation of the AgI-precipitate in KI solutions were carried out as follows. A cylindrical glass vessel containing 1 gr. of AgI (powdered in an agate mortar) and 25 c.c. KI solution of a definite concentration was carefully stoppered and placed in a shaking machine for 20 minutes. The disperse system, obtained after shaking, was kept in a dark room. In Fig. 4 are represented graphically some of the results obtained by the author (the coordinates for the curves are $\sqrt{C}$ and quantities of AgI dispergated).

2. Complex Solubilities and the Dispergation Curves of AgI in Aqueous Acetone Solutions of KI. The same methods of investigation as those described in paragraph 1 have been employed. The results obtained are graphically represented in Figs. 5*a*, 5*b* and 6.

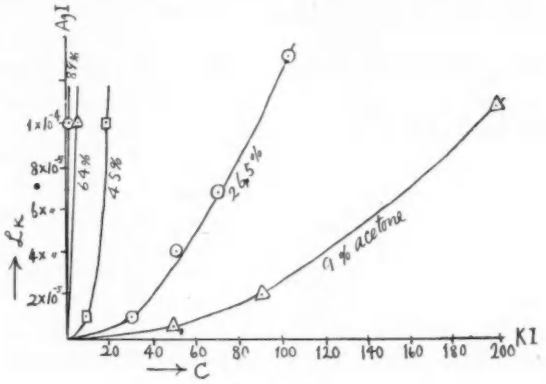


Fig. 5*a*.

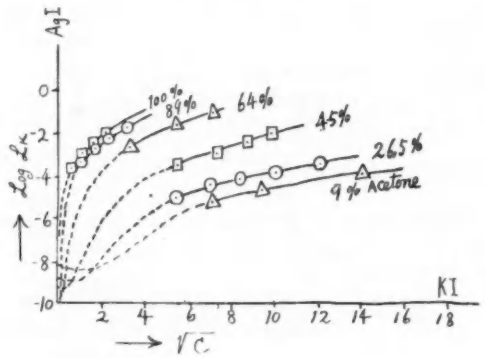


Fig. 5*b*.

When acetone is diluted with water, the strong fall in the complex solubility must correspond (see P. P. von Weimarn, Preface) to a strong increase of the dielectric constant in the acetone-aqueous mixtures, when the concentration of acetone is lowered. As is clear from the following Table such increase of the dielectric constant actually takes place.

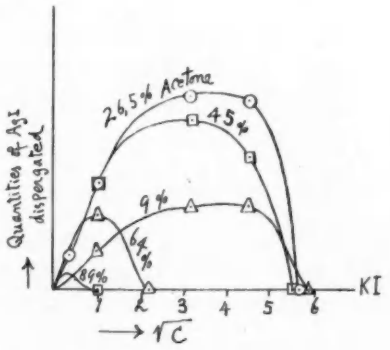


Fig. 6. (After one month)

Table 1.

Wt. % acetone	Dielect. const (19°C.)	Wt. % ethyl alcohol	Dielect. const. (20°C.)
0.	81.8	0.	81.9
25.0	67.7	—	—
50.0	51.2	50.0	49.4
80.0	32.2	80.0	34.1
100.0	20.7	100.0	26.5

Summary.

In this paper is given a graphical representation of quantitative data pertaining to:

1. The complex solubility of the AgI-precipitate in aqueous ethyl alcohol solutions of KI.
2. The dispergation process in the same solutions.
3. The complex solubility of the AgI-precipitate in aqueous acetone solutions of KI.
4. The dispergation process in the same solutions.

I wish to express here to Professor P.P. von Weimarn my sincere gratitude for suggesting the theme for these investigations.

January 1931. Dispersoidological Department of the Imperial Industrial Research Institute of Osaka.

ON THE COMPOSITION OF THE CYANIDE COMPLEX RADICAL OF METALS. PART II. CADMIUM CYANIDE COMPLEX RADICAL.

By Kosaku MASAKI.

Received January 26, 1931. Published February 28, 1931.

P. Walden[1] and V. Tafeln[2] stated that when a cadmium cyanide is dissolved in a solution of potassium cyanide, the molal ratio of combined cyanide to cadmium is four to one, corresponding to the formula $Cd(CN)_4^{--}$.

(1) *Z. anorg. Chem.*, **23** (1900), 375.
(2) *Ber.*, **35** (1902), 2668.

It may be due to the fact that the simplest of the double salts of potassium cyanide and cadmium cyanide is $2KCN \cdot Cd(CN)_2$.

Books of analytical chemistry[1] describe the following facts. By adding potassium cyanide to a solution of a cadmium salt, it produces white precipitate of amorphous cadmium cyanide and this cyanide is soluble in excess of the reagent.

$$Cd^{++} + 2CN^- \rightarrow Cd(CN)_2$$
$$Cd(CN)_2 + 2CN^- \rightarrow Cd(CN)_4^{--}$$

V. Tafeln[2] also stated that when a cadmium sulfocyanide is dissolved in a solution of potassium sulfocyanide, it produces potassium cadmium sulfocyanide, the formula of which is $Cd(CNS)_2 \cdot 2KCNS \cdot 2H_2O$, and moreover showed that there are the following complex compounds of cadmium.

(1) $Cd(CNS)_3M$ (2) $Cd(CNS)_4M_2$ (3) $Cd(CNS)_6M_4$

Composition of the Cadmium Cyanide Ion. In the present investigation, a simple titration method was used for the determination of the ratio of combined cyanide to cadmium in the complex ion. The method has already been described in the case of silver cyanide.[3] The results are shown in the following tables.

Table 1.

Sodium Cyanide and Cadmium Cyanide.

Cadmium mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre		Ratio combined cyanide to cadmium
		Apparent	Actual*	
—	2.51344	—	—	—
0.16181	2.20600	0.30744	0.46925	2.90
0.15809	2.20516	0.30828	0.46637	2.95
0.13924	2.23496	0.27848	0.41772	3.00
0.08626	2.34437	0.16907	0.25533	2.96
0.03679	2.43986	0.07358	0.11037	3.00
0.02231	2.46772	0.04572	0.06803	3.05
0.01565	2.48057	0.03287	0.04852	3.10
—	1.48376	—	—	—
0.17050	1.16264	0.32112	0.49162	2.88
0.12759	1.21801	0.26575	0.39334	3.08
0.08714	1.29552	0.18824	0.27538	3.16
0.05070	1.37303	0.11073	0.16143	3.07

* The actual concentration of combined cyanide is equal to the apparent concentration plus the concentration of cadmium.

(1) For example, Treadwell, "Lehrbuch der analytischen Chemie," Vol. 1.
(2) *Z. anorg. Chem.*, **37** (1903), 447.
(3) This Bulletin, **4** (1929), 190.

The cadmium cyanide, $Cd(CN)_2$, has been prepared by decomposing barium cyanide with cadmium sulphate. It crystallizes in small colourless rhombic prisms. The barium cyanide, $Ba(CN)_2 \cdot 2H_2O$, has been obtained by passing hydrocyanic acid into a solution of barium hydroxide, the hydrocyanic acid being obtained by boiling the mixture of potassium ferrocyanide solution and sulphuric acid with the addition of cuprous chloride to decompose completely, thus:

$$K_4Fe(CN)_6 + 3H_2SO_4 = 6HCN + FeSO_4 + 2K_2SO_4$$

Table 2.

Sodium Cyanide and Cadmium Sulphate.

Cadmium mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre	Ratio
—	1.82148	—	—
0.17895	1.30431	0.51717	2.89
0.12013	1.46710	0.35438	2.95
0.08544	1.56089	0.26059	3.05
0.05608	1.64268	0.17880	3.01
—	0.50935	—	—
0.08455	0.26021	0.24914	2.94
0.07383	0.29343	0.21593	2.92
0.06254	0.32111	0.18824	3.00
0.05154	0.35433	0.15502	3.00

Table 3.

Sodium Cyanide and Cadmium Chloride.

Cadmium mol per litre	Free cyanide mol per litre	Combined cyanide mol per litre	Ratio
—	1.82148	—	—
0.45695	0.53745	1.28403	2.81
0.27383	1.01368	0.80780	2.95
0.10658	1.49854	0.32294	3.03
—	1.48376	—	—
0.23133	0.80831	0.67545	2.91
0.15305	0.98548	0.49828	3.25
0.09789	1.17736	0.30640	3.13
0.05095	1.32989	0.15387	3.02

The cadmium sulphate and cadmium chloride which had been purified by recrystallization were used in these cases.

In all the above solutions the molal ratio of the combined cyanide to cadmium is three to one, indicating the formula to be $Cd(CN)_3^-$.

Stability of the Cadmium Cyanide Ion. There is, in the literature, no available information on the concentration of cadmium ion in cadmium cyanide solutions.

The author determined the potential differences between a cadmium electrode and various solutions of cadmium cyanide in sodium cyanide. The solutions used in these measurements were made by dissolving the appropriate amounts of pure cadmium cyanide in 50 c.c. of 0.77762 mol sodium cyanide solution. The electromotive force measurements were made at 25°C. by connecting a normal calomel electrode, through a saturated potassium chloride salt bridge, with an electrode of pure cadmium wire immersed directly in the solution, which being constantly stirred. The measured potentials remained constant over one hour. The data are summarized in Table 4.

Table 4.

$Cd(CN)_3^-$	CN^-	E	E_w	Cd^{++}	K
0.08920	0.22327	1.1567	0.8745	1.47×10^{-17}	5.45×10^{17}
0.07348	0.23097	1.1799	0.8977	1.12×10^{-17}	5.32×10^{17}
0.05502	0.24124	1.1851	0.9029	7.45×10^{-18}	5.26×10^{17}
0.02712	0.25661	1.1971	0.9149	2.90×10^{-18}	5.53×10^{17}

In Table 4, E is the measured electromotive force, and E_w is the potential of the cadmium electrode referred to the normal hydrogen electrode, taking the value for the single potential of the normal calomel electrode as -0.2822 volt.[1] The cadmium ion concentration, c, was found by the next equation

$$E_w = E_0 - 0.0295 \log c,$$

where E_0 is the standard electrode potential of the cadmium ion—cadmium electrode and is given by Lewis and associates as 0.3976 volt.[2] From the calculated value of (Cd^{++}), K can be determined from the expression:

(1) *J. Am. Chem. Soc.*, **42** (1920), 1128.
(2) Lewis and Randall, "Thermodynamics" (1923), p. 433.

$$K=\frac{Cd(CN)_3^-}{(Cd^{++})(CN^-)^3}$$

The fact that K remaines constant is an added evidence for the formula $Cd(CN)_3^-$.

Conclusion. The composition of the cadmium cyanide complex ion is probably $Cd(CN)_3^-$ at all concentrations.

The author wishes to express his appreciation to Prof. W.D. Bonner of the University of Utah, U.S.A., who suggested this research, and his best thanks to Prof. J. Sameshima and also to Prof. M. Yokoyama for the kind advice.

Yokohama Higher Technical School,
Yokohama.